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(21) International Application Number: <b>PCT/US99/06373</b>  (22) International Filing Date: 24 March 1999 (24.03.99)  (30) Priority Data: 09/080,619 18 May 1998 (18.05.98) US 09/080,629 18 May 1998 (18.05.98) US  (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/080,629 (CON) Filed on 18 May 1998 (18.05.98)  (71) Applicant (for all designated States except US): <b>PHILLIPS PETROLEUM COMPANY [US/US]; 4th and Keeler, Bartlesville, OK 74004 (US).</b>  (72) Inventors; and (75) Inventors/Applicants (for US only): <b>MCDANIEL, Max, P. [US/US]; 1601 Melmart Drive, Bartlesville, OK 74006 (US). BENHAM, Elizabeth, A. [US/US]; 431 Shannon, Bartlesville, OK 74006 (US). MARTIN, Shirley, J. [US/US]; 636 S.E. Kenwood Drive, Bartlesville, OK 74006 (US). COLLINS, Kathy, S. [US/US]; 3915 Silver Lake Drive, Bartlesville, OK 74006 (US). SMITH, James, L. [US/US];</b>		1879 Putnam, Bartlesville, OK 74006 (US). <b>HAWLEY, Gil, R. [US/US]; 1022 N. Wyandotte, Dewey, OK 74029 (US). WITTNER, Christopher, E. [US/US]; Route 1, Box 413, Bartlesville, OK 74006 (US). JENSEN, Michael, D. [US/US]; 2008 Skyline Place, Bartlesville, OK 74006 (US). JOHNSON, Marvin, M. [US/US]; 4413 S.E. Woodland Road, Bartlesville, OK 74006 (US).</b>  (74) Agents: <b>RICHARDS, John; Ladas &amp; Parry, 26 West 61st Street, New York, NY 10023 (US) et al.</b>  (81) Designated States: <b>AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b>  <b>Published</b> With international search report.	
(54) Title: <b>CATALYST COMPOSITION FOR POLYMERIZING MONOMERS</b>			
(57) Abstract  This invention provides compositions that are useful for polymerizing at least one monomer comprising: 1) a treated solid oxide compound produced by contacting at least one solid oxide with at least one electron-withdrawing anion source, 2) a metallocene compound of group IVA, 3) an organoaluminium compound.			

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CATALYST COMPOSITION FOR POLYMERIZING MONOMERSFIELD OF THE INVENTION

This invention is related to the field of catalyst compositions that can be used to polymerize monomers into at least one polymer.

5 BACKGROUND OF THE INVENTION

The production of polymers is a multi-billion dollar business. This business produces billions of pounds of polymers each year. Millions of dollars have been spent on developing technologies that can add value to this business.

One of these technologies is called metallocene catalyst technology.

10 Metallocene catalysts have been known since about 1960, however, their low productivity did not allow them to be commercialized. About 1975, it was discovered that contacting one part water with two parts trimethylaluminum to form methyl aluminoxane, and then contacting such methyl aluminoxane with a metallocene compound, formed a metallocene catalyst that had greater activity. However, it was soon

15 realized that large amounts of expensive methyl aluminoxane were needed to form an active metallocene catalyst. This has been a significant impediment to the commercialization of metallocene catalysts.

Borate compounds have been use in place of large amounts of methyl aluminoxane. However, this is not satisfactory, since borate compounds are very

20 sensitive to poisons and decomposition, and can also be very expensive.

It should also be noted that having a heterogeneous catalyst is important. This is because heterogeneous catalysts are required for most modern commercial polymerization processes. Furthermore, heterogeneous catalysts can lead to the formation of substantially uniform polymer particles that have a high bulk

25 density. These types of substantially uniform particles are desirable because they improve the efficiency of polymer production and transportation. Efforts have been made to produce heterogeneous metallocene catalysts, however, these catalysts have not been entirely satisfactory.

Therefore, the inventors provide this invention to solve these problems.

30 SUMMARY OF THE INVENTION

The invention provides a process that produces a composition that can be used to polymerize monomers into at least one polymer.

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The invention also provides said composition.

The invention further provides a process to polymerize monomers into at least one polymer using said composition.

The invention also deals with a manufacture comprising at least one  
5 said polymer and a machine comprising at least one said manufacture.

In accordance with one aspect of this invention, a process to produce a composition is provided. Said process comprises (or optionally, consists essentially of, or consists of) contacting an organometal compound, a treated solid oxide compound, and an organoaluminum compound to produce said composition, wherein  
10 said composition consists essentially of (or optionally, consists of) a post-contacted organometal compound, a post-contacted treated solid oxide compound, and optionally, a post-contacted organoaluminum compound.

In accordance with a second aspect of this invention, a composition of matter is provided. Said composition consists essentially of a post-contacted organo-  
15 metal compound, a post-contacted treated solid oxide compound, and optionally, a post-contacted organoaluminum compound.

In accordance with a third aspect of this invention, a process to polymerize monomers into at least one polymer using said composition is provided. Said process comprises contacting said composition with monomers.

20 In accordance with a fourth aspect of this invention a manufacture is provided. Said manufacture comprises at least one said polymer.

In accordance with a fifth aspect of this invention a machine is provided. Said machine comprises at least two said manufactures.

25 These objects, and other objects, will become more apparent to those with ordinary skill in the art after reading this disclosure.

It should be noted that the phrase "consisting essentially of" means that the only other items (such as, for example, process steps, and other compounds) included within the scope of the claims are those items that do not have an adverse effect on the basic and novel characteristics of the claimed invention.

30 It should also be noted that the phrase "consisting of" means that the no other items (such as, for example, process steps, and other compounds) are included within the scope of the claims, except items that are impurities ordinarily

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associated with a composition, or items that are process steps ordinarily associated with a process.

#### DETAILED DESCRIPTION OF THE INVENTION

Organometal compounds used in this invention have the following  
5 general formula.

#### FORMULA ONE: $(X^1)(X^2)(X^3)(X^4)M^1$

In this formula,  $M^1$  is selected from the group consisting of titanium, zirconium, and hafnium. Currently, it is most preferred when  $M^1$  is zirconium.

In this formula  $(X^1)$  is independently selected from the group  
10 consisting of (hereafter "Group OMC-I") cyclopentadienyls, indenyls, fluorenyls, substituted cyclopentadienyls, substituted indenyls, such as, for example, tetrahydro-indenyls, and substituted fluorenyls, such as, for example, octahydrofluorenyls.

The substituents on the substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, can be aliphatic groups, cyclic groups,  
15 combinations of aliphatic and cyclic groups, and organometallic groups, as long as these groups do not substantially, and adversely, affect the polymerization activity of the composition. Additionally, hydrogen can be a substituent.

Suitable examples of aliphatic groups are hydrocarbyls, such as, for example, paraffins and olefins. Suitable examples of cyclic groups are cycloparaffins,  
20 cycloolefins, cycloacetylenes, and arenes. Additionally, alkylsilyl groups where each alkyl contains 1-12 carbon atoms, alkyl halide groups where each alkyl contains 1-12 carbon atoms, or halides, can also be used.

Suitable examples of such substituents are methyl, ethyl, propyl, butyl, tert-butyl, isobutyl, amyl, isoamyl, hexyl, cyclohexyl, heptyl, octyl, nonyl, decyl,  
25 dodecyl, 2-ethylhexyl, pentenyl, butenyl, phenyl, chloro, bromo, and iodo.

In this formula  $(X^3)$  and  $(X^4)$  are independently selected from the group consisting of (hereafter "Group OMC-II") halides, aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, as long as these groups do not substantially, and adversely, affect the polymerization  
30 activity of the composition.

Suitable examples of aliphatic groups are hydrocarbyls, such as, for example, paraffins and olefins. Suitable examples of cyclic groups are cycloparaffins,

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cycloolefins, cycloacetylenes, and arenes. Currently, it is preferred when (X<sup>3</sup>) and (X<sup>4</sup>) are selected from the group consisting of halides and hydrocarbyls, where such hydrocarbyls have from 1 to 10 carbon atoms. However, it is most preferred when (X<sup>3</sup>) and (X<sup>4</sup>) are selected from the group consisting of fluoro, chloro, and methyl.

5           In this formula, (X<sup>2</sup>) can be selected from either Group OMC-I or Group OMC-II.

          When (X<sup>2</sup>) is selected from Group OMC-I, it should be noted that (X<sup>1</sup>) and (X<sup>2</sup>) can be joined with a bridging group, such as, for example, aliphatic bridging groups, cyclic bridging groups, combinations of aliphatic and cyclic bridging groups,  
10   and organometallic bridging groups, as long as the bridging group does not substantially, and adversely, affect the polymerization activity of the composition.

          Suitable examples of aliphatic bridging groups are hydrocarbyls, such as, for example, paraffins and olefins. Suitable examples of cyclic bridging groups are cycloparaffins, cycloolefins, cycloacetylenes, and arenes. Additionally, it should  
15   be noted that silicon and germanium are also good bridging units.

          Various processes are known to make these compositions. See, for example, U.S. Patents 4,939,217; 5,210,352; 5,436,305; 5,401,817; 5,631,335, 5,571,880; 5,191,132; 5,480,848; 5,399,636; 5,565,592; 5,347,026; 5,594,078; 5,498,581; 5,496,781; 5,563,284; 5,554,795; 5,420,320; 5,451,649; 5,541,272;  
20   5,705,478; 5,631,203; 5,654,454; 5,705,579; and 5,668,230.

          Specific examples of such compositions are as follows:

          bis(cyclopentadienyl) hafnium dichloride;  
          bis(cyclopentadienyl) zirconium dichloride;  
          [ethyl(indenyl)<sub>2</sub>] hafnium dichloride;  
25   [ethyl(indenyl)<sub>2</sub>] zirconium dichloride;  
          [ethyl(tetrahydroindenyl)<sub>2</sub>] hafnium dichloride;  
          [ethyl(tetrahydroindenyl)<sub>2</sub>] zirconium dichloride;  
          bis(n-butylcyclopentadienyl) hafnium dichloride;  
          bis(n-butylcyclopentadienyl) zirconium dichloride;  
30   ((dimethyl)(diindenyl) silane) zirconium dichloride;  
          ((dimethyl)(diindenyl) silane) hafnium dichloride;  
          ((dimethyl)(ditetrahydroindenyl) silane) zirconium dichloride;

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((dimethyl)(di(2-methyl indenyl)) silane) zirconium dichloride; and  
bis(fluorenyl) zirconium dichloride.

Organoaluminum compounds have the following general formula.

FORMULA TWO:  $Al(X^5)_n(X^6)_3-n$

5           In this formula ( $X^5$ ) is a hydrocarbyl having from 1-20 carbon atoms.  
Currently, it is preferred when ( $X^5$ ) is an alkyl having from 1 to 10 carbon atoms.  
However, it is most preferred when ( $X^5$ ) is selected from the group consisting of  
methyl, ethyl, propyl, butyl, and isobutyl.

10           In this formula ( $X^6$ ) is a halide, hydride, or alkoxide. Currently, it is  
preferred when ( $X^6$ ) is independently selected from the group consisting of fluoro and  
chloro. However, it is most preferred when ( $X^6$ ) is chloro.

          In this formula "n" is a number from 1 to 3 inclusive. However, it is  
preferred when "n" is 3.

Examples of such compounds are as follows:

15           trimethylaluminum;  
          triethylaluminum;  
          tripropylaluminum;  
          diethylaluminum ethoxide;  
          tributylaluminum;  
20           triisobutylaluminum hydride;  
          triisobutylaluminum; and  
          diethylaluminum chloride.

Currently, triethylaluminum is preferred.

25           The treated solid oxide compounds are compounds that have had their  
Lewis acidity increased. It is preferred when said treated solid oxide compound  
comprises oxygen and at least one element selected from the group consisting of  
groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 (new notation) of the periodic  
table, including lanthanides and actinides (See Hawley's Condensed Chemical  
Dictionary, 11th Edition). However, it is preferred when the element is selected from  
30           the group consisting of Al, B, Be, Bi, Cd, Co, Cr, Cu, Fe, Ga, La, Mn, Mo, Ni, Sb,  
Si, Sn, Sr, Th, Ti, V, W, P, Y, Zn and Zr. It is important that these treated solid  
oxide compounds have electron withdrawing ability, while not wanting to be bound

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by theory, it is believed that a treated solid oxide compound should have a higher Lewis acidity compared to the untreated solid oxide compound. However, it is hard to accurately measure the Lewis acidity of these treated, and untreated solid oxide compounds so other methods have been used. Currently, comparing the activities of treated, and untreated solid oxide compounds under acid catalyzed reactions is preferred.

Treated solid oxide compounds can be produced in a variety of ways, such as, for example, by gelling, co-gelling, or impregnation of one compound onto another, followed by calcination.

10 In general, it is preferred to contact at least one solid oxide compound, such as, for example, alumina, zirconia, titania, and mixtures thereof or with mixture with other solid oxides such as, for example, silica alumina, with at least one electron-withdrawing anion source compound and optionally with at least one metal salt compound, to form a first mixture, followed by calcining this first mixture to form a treated solid oxide compound. In the alternative, a solid oxide compound, an electron-withdrawing anion source compound and optionally said metal salt compound can be contacted and calcined simultaneously. In another alternative, the metal salt compound and the electron-withdrawing anion source can be the same compound.

20 The metal salt compound is any compound that increases the Lewis acidity of the solid oxide under the conditions given herein for producing the treated solid oxide compound. It is preferred when said metal in said metal salt is selected from the group consisting of groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 (new notation) of the Periodic Table, including lanthanides and actinides (See Hawley's Condensed Chemical Dictionary, 11th Edition). However, it is preferred when the element is selected from the group consisting of Al, B, Be, Bi, Cd, Co, Cr, Cu, Fe, Ga, La, Mn, Mo, Ni, Sb, Si, Sn, Sr, Th, Ti, V, W, P, Y, Zn and Zr.

25 The electron-withdrawing anion source compound is any compound that increases the Lewis acidity of the solid oxide under the conditions given herein for producing the treated solid oxide compound. These electron-withdrawing anion source compounds increase the Lewis acidity of the solid oxide by contributing to the formation of an electron withdrawing anion, such as, for example, sulfates, halides,



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and triflate. It should be noted that one or more different electron withdrawing anions can be used. Furthermore, it is believed that metal salt compounds enhance the polymerization activity of the composition.

The acidity of the solid oxide compound can be further enhanced by using two, or more, metal salts and/or electron-withdrawing anion source compounds in two, or more, separate contacting steps. An example of such a process is contacting at least one solid oxide compound with a first electron-withdrawing anion source compound to form a first mixture, followed by calcining this first mixture, followed by contacting with a second electron-withdrawing anion source compound to form a second mixture, followed by calcining said second mixture to form a treated solid oxide compound. It should be noted that the first and second electron-withdrawing anion source compounds can be the same, but are preferably different.

Suitable examples of solid oxide compounds include, but are not limited to,  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{CdO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MoO}_3$ ,  $\text{NiO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{SiO}_2$ ,  $\text{SnO}_2$ ,  $\text{SrO}$ ,  $\text{ThO}_2$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ; and mixtures thereof, such as, for example, silica-alumina and silica-zirconia. It should be noted that solid oxide compounds that comprise Al-O bonds are currently preferred.

It is preferred that the solid oxide compound is also calcined. This calcining can be conducted in an ambient atmosphere, preferably a dry ambient atmosphere, at a temperature in the range of about  $200^\circ\text{C}$  to about  $900^\circ\text{C}$ , and for a time in the range of about 1 minute to about 100 hours. Currently, temperatures from about  $400^\circ\text{C}$  to about  $800^\circ\text{C}$  and a time in the range of about 1 hour to about 10 hours, are preferred.

Treated solid oxide compounds, should have pore volumes greater than about 0.01 cc/g, preferably greater than about 0.1 cc/g, and most preferably, greater than about 1 cc/g.

Treated solid oxide compounds should have surface areas greater than about  $1 \text{ m}^2/\text{g}$ , preferably greater than  $100 \text{ m}^2/\text{g}$ , and most preferably greater than  $200 \text{ m}^2/\text{g}$ .

The compositions of this invention can be produced by contacting an organometal compound, a treated solid oxide compound, and an organo-aluminum

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compound, together. This contacting can occur in a variety of ways, such as, for example, blending. Furthermore, each of these compounds can be fed into the reactor separately, or various combinations of these compounds can be contacted together before being further contacted in the reactor, or all three compounds can be contacted together before being introduced into the reactor. Currently, one method is to first  
5 contact the organometal compound and the treated solid oxide compound together, for about 1 minute to about 24 hours, preferably, about 1 minute to about 1 hour, at a temperature from about 10°C to about 200°C, preferably about 25°C to about 100°C, to form a first mixture, and then contact this first mixture with an organoaluminum  
10 compound to form the composition. During contacting, or after contacting, the mixtures or the composition can be calcined. This calcining can be conducted in an ambient atmosphere, preferably a dry ambient atmosphere, at a temperature in the range of about 300°C to about 900°C, and for a time in the range of about 1 minute to about 100 hours. Currently, temperatures from about 500°C to about 700°C and a  
15 time in the range of about 1 hour to about 10 hours, are preferred. Currently, it is preferred to use dry nitrogen as the ambient atmosphere.

After contacting, the composition consists essentially of, (or consists of) a post-contacted organometal compound, a post-contacted treated solid oxide compound, and optionally, a post-contacted organoaluminum compound. It should be  
20 noted that the post-contacted treated solid oxide compound is the majority, by weight, of the composition. Since the exact order of contacting is not known, it is believed that this terminology best describes the composition's components.

The composition of this invention has an activity greater than a composition that uses the same organometal compound, and the same organo-  
25 aluminum compound, but uses untreated Ketjen grade B alumina (see comparative Examples 4, 5, and 6) instead of the treated solid oxide compounds of this invention. This activity is measured under slurry polymerization conditions, using isobutane as the diluent, and with a polymerization temperature of 50-150°C, and an ethylene pressure of 400-800 psig. The reactor should have substantially no indication of any  
30 wall scale, coating or other forms of fouling.

However, it is preferred if the activity is greater than 100 grams polyethylene per gram of treated solid oxide compound per hour (hereafter

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"gP/(gS•hr)"), more preferably greater than 250, even more preferably greater than 500, even more preferably greater than 1000, and most preferably greater than 2000. This activity is measured under slurry polymerization conditions, using isobutane as the diluent, and with a polymerization temperature of 90°C, and an ethylene pressure  
5 of 550 psig. The reactor should have substantially no indication of any wall scale, coating or other forms of fouling.

These compositions are often sensitive to hydrogen and sometimes incorporate comonomers well, and usually produce polymers with a low HLMI/MI ratio.

10 One of the important aspects of this invention is that no aluminoxane needs to be used in order to form the composition. This also means that no water is needed to help form such aluminoxanes. This is beneficial because water can sometimes kill a polymerization process. Additionally, it should be noted that no borate compounds need to be used in order to form the composition. In summary, this  
15 means that the composition, which is heterogenous, and which can be used for polymerizing monomers, can be easily and inexpensively produced because of the substantial absence of any aluminoxane compounds or borate compounds. Additionally, no organo-chromium needs to be added, nor any  $MgCl_2$  needs to be added to form the invention.

20 The monomers useful in this invention, are unsaturated hydrocarbons having from 2 to 20 carbon atoms. Currently, it is preferred when the monomer is selected from the group consisting of ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and mixtures thereof. However,  
25 when a homopolymer is desired, it is most preferred to use ethylene, or propylene, as the monomer. Additionally, when a copolymer is desired, it is most preferred to use ethylene and hexene as the monomers.

Processes that can polymerize monomers into polymers are known in the art, such as, for example, slurry polymerization, gas phase polymerization, and  
30 solution polymerization. It is preferred to perform a slurry polymerization in a loop reactor. Furthermore, it is even more preferred to use isobutane as the diluent in a slurry polymerization. Examples of such technology can be found in U.S. Patents

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4,424,341; 4,501,885; 4,613,484; 4,737,280; and 5,597,892.

It should be noted that under slurry polymerization conditions these compositions polymerize ethylene alone, or ethylene with a 1-olefin, or propylene very well. In particular, the compositions used in this process produce good quality polymer particles without substantially fouling the reactor. When the composition is to be used in a loop reactor under slurry polymerization conditions, it is preferred when the particle size of the solid mixed oxide compound is in the range of about 10 to about 1000 microns, preferably 25 to 500 microns, and most preferably, about 50 to about 200 microns, for best control during polymerization.

After the polymers are produced, they can be formed into various manufactures, such as, for example, household containers and utensils, drums, fuel tanks, pipes, geomembranes, and liners. Various processes can form these manufactures. Usually, additives and modifiers are added to the polymer in order to provide desired effects. It is believed that by using the invention described herein, manufactures can be produced at a lower cost, while maintaining most, if not all, of the unique properties of polymers produced with metallocene catalysts.

Additionally, these manufactures can be part of a machine, such as, for example, a car, so that the weight of the car will be less, with the attendant benefits thereof.

#### EXAMPLES

These examples provide additional information to a person skilled in the art. These examples are not meant to be construed as limiting the scope of the claims.

#### DESCRIPTION OF THE POLYMERIZATIONS RUNS

All polymerization runs were conducted in a steel reactor that had a volume of 2.2 liters. This reactor was equipped with a marine stirrer. During the polymerizations this stirrer was set to run at 400 rpm. This reactor was also surrounded by a steel jacket that was connected to a steel condenser. The steel jacket contained methanol that was boiling. The boiling point of the methanol was controlled by varying the nitrogen pressure that was applied to the steel condenser and the steel jacket. This control method permitted precise temperature control ( $\pm 0.5^{\circ}\text{C}$ ).

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First, a treated, or untreated, solid oxide compound was charged, under nitrogen, to the reactor, which was dry. Second, organometal compound solution was added to the reactor by syringe. Third, 0.6 liters of isobutane was charged to the reactor. Fourth, organoaluminum compound was added midway during the isobutane addition. Fifth, 0.6 liters of isobutane was charged to the reactor. Sixth, ethylene was added to the reactor to equal 550 psig pressure. Seventh, the reactor was heated to 90°C. This pressure was maintained during the polymerization. During polymerization, stirring continued for the specified time. Activity was determined by recording the flow of ethylene into the reactor to maintain pressure. Eighth, after the specified time, the ethylene flow was stopped and the reactor slowly depressurized. Ninth, the reactor was opened to recover a granular polymer powder.

In all inventive runs, the reactor was clean with no indication of any wall scale, coating or other forms of fouling. The polymer powder was removed and weighed. Activity was specified as grams of polymer produced per gram of treated, or untreated, solid oxide compound charged per hour.

In some cases the treated solid oxide compound and the organometal compound were first pre-contacted, in the reactor, for about half an hour at 90°C in one liter of isobutane before the organoaluminum compound and ethylene were added to the reactor.

20

#### PREPARATION OF SOLID OXIDES

Silica, grade 952, having a pore volume of 1.6 cc/g and a surface area of about 300 square meters per gram was obtained from W.R.Grace. About 10 grams of this material was placed in a 1.75 inch quartz tube, which was fitted at the bottom with a sintered quartz. While the silica was supported on the disk, dry air was blown up through the disk at the linear rate of about 1.6 to 1.8 standard cubic feet per hour. An electric furnace around the quartz tube was then turned on and the temperature was raised at the rate of 400°C per hour to a temperature of 600°C. At that temperature, the silica was allowed to fluidize for three hours in the dry air. Afterward, the silica was collected and stored under dry nitrogen.

30

Some alumina samples were also prepared by the procedure described in the silica preparation. A commercial alumina sold by AKZO Company as Ketjen grade B alumina, having a pore volume of about 1.78 cc/g and a surface area of

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around 340 square meters per gram, was obtained. The temperatures used in the preparation of these aluminas were 400°C, 600°C, and 800°C.

A silica-alumina was also obtained from W.R.Grace (MS 13-110 containing 13% alumina and 87% silica). This silica-alumina had a pore volume of 1.2 cc/g and a surface area of about 300 square meters per gram. This silica-alumina was prepared as described in the silica preparation. The temperature used in the preparation of this silica-alumina was 600°C.

A silica-titania was obtained by co-gellation as described in U.S. Patent 3,887,494 ("Deitz"). Titanyl sulfate was dissolved in concentrated sulfuric acid, to form a first mixture. Afterwards, a sodium silicate solution was slowly added, with vigorous stirring, to this first mixture, to form a second mixture. When the pH of the second mixture reached about 6, this second mixture gelled into a homogenous, substantially-clear first product. This first product was then aged, at 80°C and a pH 7, for three hours, followed by washing it nine times with water, and two times in 1% ammonium nitrate, to form a second product. This second product, which was a gel, was then azeotropically dried in ethyl acetate, to form a third product. This third product contained 8% titanium. It also had a surface area of 450 square meters per gram and a pore volume of 2.0 cc/g. This silica-titania was then prepared as described in the silica preparation. The temperature use in the preparation of this silica-titania was 600°C.

An alumino-phosphate was prepared according to U.S. Patent 4,364,855 (McDaniel). Aluminum nitrate (380 grams) and mono-ammonium phosphate (94 grams) was dissolved in deionized water to form a first mixture. About 170 milliliters of ammonium hydroxide was then added to this first mixture to form a second mixture. At a pH of about 8 this second mixture gelled to form a first product. This first product was then washed twice in water, and once in n-propanol, before drying overnight at 80°C under a vacuum, to form a second product. This second product contained a phosphorus to aluminum molar ratio of 0.8, a pore volume of 2.1 cc/g, and a surface area of 250 square meters per gram. This alumino-phosphate was then prepared as described in the silica preparation. The temperature use in the preparation of this alumina-phosphate was 600°C.

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COMPARATIVE EXAMPLES 1-2

These examples demonstrate that an organometal compound contacted with an organoaluminum compound, provides little, if any, polymerization activity.

A polymerization run was made as described earlier. First, an organometal compound was added to the reactor (2 ml of bis(n-butylcyclopentadienyl) zirconium dichloride solution containing 0.5 grams per 100 ml of toluene). Second, half of the isobutane was then added to the reactor. Third, 2 ml of 15 weight percent triethyl aluminum for Example 1, or 2 ml of 25 weight percent ethyl aluminum dichloride (EADC) for Example 2, were added to the reactor. Fourth, the other half of the isobutane was added to the reactor.

Ethylene was then added to the reactor but no polymerization activity was observed. After one hour of contacting, the reactor was depressurized and opened.

In each case, no polymer was found. These results are shown in Table-I.

COMPARATIVE EXAMPLES 3-9

These examples demonstrate that contacting a solid oxide compound, with an organometal compound, and with an organoaluminum compound, provided little, if any, polymerization activity.

Each of the solid oxide compounds described earlier was added to the reactor, followed by an organometal compound (2 ml of bis(n-butylcyclopentadienyl) zirconium dichloride solution (0.5 grams per 100 ml of toluene), and then the organoaluminum compound (triethylaluminum). These examples are shown in Table-I.

The first two examples show that contacting an organometal compound with an organoaluminum compound provides little, if any, polymerization activity. The silica example produced almost no polymer. Alumina, which is regarded as more acidic than silica, produced more polymer, but still the activity was very low. The aluminophosphate, silica-alumina, and silica-titania supports exhibited only marginal activity. Activity is expressed in Table-I as gP/(gS•hr).

COMPARATIVE EXAMPLE 10

A solution was made of 244 grams of ammonium sulfate dissolved in water to equal 437 mls total. Then 100 mls of this solution was impregnated onto

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33.2 grams of W.R.Grace grade 952 silica. The wet mixture was dried in a vacuum oven at 110°C for 12 hours. This is equivalent to 12.7 mmol of sulfate per gram of silica. The dried material was ground through a 35 mesh screen, then calcined in air at 400°C according to the procedure described earlier. It was found to have a pore volume of 1.22 cc/g and a surface area of 223 square meters per gram. A sample of this material was then tested for ethylene polymerization activity as described earlier. It produced no polymer. This experiment is shown in Table II as Example 10.

#### EXAMPLES 11-12

122 mls of the above ammonium sulfate solution was impregnated onto 40.6 grams of Ketjen grade B alumina. The wet mixture was dried in a vacuum oven at 110°C for 12 hours. This is equivalent to 12.7 mmol of sulfate per gram of uncalcined alumina. The dried material was then ground through a 35 mesh screen and calcined in air at 400°C according to the procedure described above. It was found to have a pore volume of only 0.25 cc/g and a surface area of only 38 square meters per gram. A sample of this material was then tested for ethylene polymerization activity as described earlier. Despite the very low porosity it still produced 33 g/g/h of polymer. This experiment is shown in Table II as Example 11.

This same material was then calcined again in air at 750°C as described earlier, and retested for polymerization activity. This time it provided 583 g/g/h of polymer. This is quite remarkable considering the very low surface area. The polymer was found to have a melt index of 0.15 and a high load melt index of 3.24. This experiment is shown in Table II as Example 12.

#### EXAMPLE 13 A, B, C

Ketjen B alumina was first calcined in air at 600°C as described earlier. Then 11.1 grams of this material was slurried with 30 mls of isopropanol mixed with 1.73 grams of sulfuric acid. This is equivalent to 1.6 mmol of sulfate per gram of calcined alumina. The isopropanol was then evaporated off under nitrogen with heat. The dry solid was then calcined in air at 550°C as described earlier. A sample of this material was then tested for ethylene polymerization. It yielded 1387 g/g/h of polymer. This experiment is shown in Table II as Example 13A.

The earlier procedure Ketjen B alumina was first calcined in air at 600°C, then 5.9 grams of this material was slurried with 15 mls of isopropanol mixed



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with 0.453 grams of sulfuric acid. This is equivalent to 1.6 mmol of sulfate per gram of calcined alumina. The isopropanol was then evaporated off under nitrogen with heat. The dry solid was then calcined in air at 550°C as described earlier. It was found to have a pore volume of 0.93 cc/g and a surface area of 205 square meters per gram. A sample of this material was then tested for ethylene polymerization. It yielded 324 g/g/h of polymer. This experiment is shown in Table II as Example 13B.

This material was then calcined again at 800°C for three hours in air as described earlier. It was found to have a pore volume of 1.03 cc/g and a surface area of 236 square meters per gram. It provided activity of 58 g/g/h polymer. This experiment is shown in Table II as Example 13C.

#### EXAMPLES 14 A, B and 15

The procedure of Example 11 was repeated except that 33.14 grams of Ketjen B alumina was impregnated with 11.60 grams of ammonium sulfate and then it was calcined at 550C. The results of testing are shown in Table II as Example 14A. During this run the sulfated alumina and metallocene were precontacted in the reactor for 32 minutes at 90C before other ingredients were introduced to begin the run. Polymer produced in this run was found to have a MI of 0.21, a HLMI of 3.5, giving a shear ratio of 16.7. Gel permeation chromatography of the polymer indicated Mw=168,000, Mn=67,900 and Mw/Mn=2.5. After calcining the sulfated alumina was found to have a surface area of 284 square meters per gram and a pore volume of 0.67 cc/g and an average pore radius of 94 angstroms.

The above sulfated alumina (14A) was then calcined in air at 650C for three hours and tested again for polymerization. Again the sulfated alumina and the metallocene were precontacted for 30 minutes at 90C. Details of the run are shown in Table II as Example 14B. This material was found to have a surface area of 305 square meters per gram, a pore volume of 0.9 cc/g, and an average pore volume of 110 angstroms.

Another sample of sulfated alumina was made by the same procedure as Example 14A except that 26.9 g of Ketjen B alumina was impregnated with 5.41 g of ammonium sulfate. Calcination was at 550C. It was found to have a surface area of 352 square meters per gram, a pore volume of 0.93 cc/g, and an average pore

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radius of 106 angstroms. Details of the polymerization are given in Table II as Example 15.

#### COMPARATIVE EXAMPLE 16

A solution of 2.0 grams of concentrated sulfuric acid in 200 mls of isopropanol was made. Ketjen B alumina was calcined in air at 600°C as described earlier. Then 6.34 grams of this material was slurried with 16 mls of the solution. This is equivalent to 0.26 mmol of sulfate per gram of calcined alumina. The isopropanol was then evaporated off under nitrogen with heat. The dry solid was then calcined in air at 500°C as described earlier. It was found to have a pore volume of 0.95 cc/g and a surface area of 213 square meters per gram. A sample of this material was then tested for ethylene polymerization. It yielded 6 g/g/h of polymer. This experiment is shown in Table II as Example 16.

#### EXAMPLE 17

A silica-alumina was obtained from W.R.Grace under the commercial name of MS13-110. It's properties and activity have already been described earlier. It was impregnated with sulfuric acid as described above in Example 16 to contain 1.6 mmol sulfate per gram. It was then calcined in air at 600°C as described earlier. A sample of this material was then charged to the reactor along with the metallocene and isobutane and stirred for 32 minutes at 90°C before ethylene was added. It yielded 82 g/g/h of polymer. This experiment is shown in Table II as Example 17.

#### EXAMPLE 18

A solution of 0.5 grams of ammonium bifluoride in 30 mls of methanol was added to 4.5 grams of Ketjen grade B alumina which had been calcined in air at 600°C as described earlier. This moistened the alumina just beyond the point of incipient wetness. This is equivalent to 3.90 mmol of fluoride per gram of calcined alumina. The methanol was then evaporated off under nitrogen with heat. The dry solid was then calcined in nitrogen at 500°C as described earlier. A sample of this material was then tested for ethylene polymerization. It yielded 927 g/g/h of polymer. This experiment is shown in Table III as Example 18.

#### EXAMPLES 19-21

The procedure described in Example 18 was repeated except that the final calcination was accomplished at 250°C, 400°C, and 600°C. Each was tested for

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polymerization activity and the results are shown in Table III as Examples 19, 20, and 21.

#### EXAMPLE 22

The procedure described in Example 18 was repeated except that  
5 uncalcined Ketjen B alumina was impregnated with 5.80 mmol per gram of fluoride. After calcination at 500°C it was tested for polymerization activity and the result are shown in Table III as Example 22.

#### EXAMPLE 23-24

W.R.Grace grade HPV alumina was calcined at 600°C in air three  
10 hours, giving a material of surface area around 500 square meters per gram and pore volume of about 2.8 cc/g. 3.36 grams of this material was heated under fluidizing nitrogen to 600°C. Then 5.0 mls of perfluorohexane was injected into the nitrogen upstream from the alumina. Over the next 15 minutes the perfluorohexane  
15 evaporated at room temperature into the nitrogen and was then carried up through the fluidizing bed of alumina, where it reacted. This exposure would be equivalent to about 55 mmol of fluoride per gram of alumina if all of the fluoride reacted (which was obviously not the case). The alumina turned black, presumably due to carbon deposited on it. This material was then tested for polymerization activity when a  
20 sample was charged to the reactor with the metallocene at 90°C. After 30 minutes of stirring, triethyl aluminum and ethylene were added and the sample was found to provide 1266 g/g/h of polymer. Details are shown in Table III as Example 23.

This material was then recalcined in air at 600°C for three hours to  
burn off residual carbon. The black color turned back to white. It was then tested for polymerization activity when a sample of it was added to the reactor along with  
25 metallocene and triethyl aluminum, followed immediately by ethylene. It provided an activity of 2179 g/g/h of polymer. Details are shown in Table III as Example 24.

#### EXAMPLES 25-26

Ketjen Grade B alumina was calcined in air for three hours at 600°C  
as described in Example 5. 9.29 grams of this alumina was charged to a dry quartz  
30 activator tube and fluidized in carbon monoxide at 600°C. Then 4.5 mls of methyl bromide was injected upstream into the carbon monoxide. During the next 30 minutes the methyl bromide was warmed with an electric heater causing it to

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evaporate and be carried by the carbon monoxide gas through the fluidizing alumina bed at 600°C. After this treatment the alumina was black, presumably from carbon deposits. A sample was tested for polymerization activity and found to give 223 g/g/h of polymer. In a second similar run it was found to give 181 g/g/h of polymer.

5 These two runs are shown in Table IV as Examples 25 and 26.

#### EXAMPLE 27

Ketjen Grade B alumina was calcined in air for three hours at 600°C as described in Example 5. 9.82 grams of this alumina was charged to a dry quartz activator tube and fluidized in carbon monoxide at 600°C. Then 1.0 mls of bromine  
10 liquid was injected upstream into the carbon monoxide which slowly evaporated and was carried through the fluidizing alumina bed at 600°C. After this treatment the alumina was white. A sample was tested for polymerization activity and found to give 106 g/g/h of polymer. This run is shown in Table IV as Example 27.

#### EXAMPLES 28-31

15 Ten mls of Ketjen Grade B alumina was calcined in air for three hours at 600°C as described in Example 5. After this calcining step, the furnace temperature was lowered to 400°C and 1.0 ml of carbon tetrachloride was injected into the nitrogen stream and evaporated upstream from the alumina bed. It was carried into the bed and there reacted with the alumina to chloride the surface. This  
20 is equivalent to approximately 15.5 mmol chloride per gram of dehydrated alumina. After this treatment the alumina was white. A sample was tested for polymerization activity. In addition to the ethylene, 50 mls of 1-hexene was also added to the reactor as a comonomer. This material gave 939 g/g/h of copolymer having the following properties: melt index of 0.63, high load melt index of 10.6, shear ratio of  
25 16.7, density of 0.9400, weight average MW of 126,000, number average MW of 50,200, and polydispersity of 2.5. This run is shown in Table V as Example 28.

This chlorided alumina was run again but without the hexene and the details are shown in Table V as Example 29. It produced 1019 g/g/h of polymer having the following properties: melt index of 0.15, high load melt index of 2.68,  
30 shear ratio of 17.9, density of 0.9493, weight average MW of 202,000, number average MW of 62,400, and polydispersity of 3.2.

In a similar experiment, 7.3 grams of Ketjen Grade B alumina already

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calcined at 600°C in air, was treated with 0.37 mls of carbon tetra-chloride vapor in nitrogen at 400°C. This is equivalent to approximately 2.4 mmol chloride per gram of calcined alumina. This material provided 146 g/g/h activity and is shown in Table V as Example 30.

5                In yet another similar experiment, the procedure of Example 29 was repeated except that 6.2 grams of 600°C calcined alumina was treated with 5.0 mls of carbon tetrachloride at 400°C, which is approximately equivalent to 37.6 mmol chloride per gram. This material yielded 1174 g/g/h activity and is shown in Table V as Example 31.

10                EXAMPLES 32-35

Three other samples of Ketjen Grade B alumina were also calcined at 600°C in air as described in the above examples and then treated with various amounts of carbon tetrachloride at various temperatures. Table V shows the results of these experiments as Examples 32, 33, and 34. In Example 33 the treatment was  
15                done in carbon monoxide gas instead of nitrogen.

The catalyst of Example 33 was retested for polymerization activity but with the following variation. Instead of charging all ingredients to the reactor and immediately starting the run, the oxide and the metallocene were charged with the isobutane first and allowed to contact each other for 37 minutes at 90°C before the  
20                cocatalyst and ethylene were added to begin the run. This run is shown in Table V as Example 35.

EXAMPLE 36

W.R.Grace Grade HPV alumina was calcined in air for three hours at 600°C, yielding a surface area of approximately 500 square meters per gram and a  
25                pore volume of about 2.8 cc/g. 5.94 grams of this alumina was then treated with 5.0 mls of carton tetrachloride in nitrogen at 600°C. Results of polymerization testing are shown in Table V as Example 36.

EXAMPLE 37

W.R.Grace Grade MS13-110 silica-alumina was calcined in air for  
30                three hours at 600°C, as described in Example 8 above. 11.2 grams then treated with 2.8 mls of carton tetrachloride in nitrogen at 600°C. Results of polymerization testing are shown in Table V as Example 37.

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EXAMPLE 38

6.96 grams of Ketjen Grade B alumina which had been calcined at 400°C in air for three hours was charged to a dry activator tube and heated under nitrogen to 400°C. 2.1 mls of silicon tetrachloride was then injected into the nitrogen upstream from the alumina. As it evaporated it was carried up through the alumina bed, reacting and chloriding the surface. When tested for polymerization activity this material provided 579 g/g/h of polymer having a melt index of 0.20, a high load melt index of 3.58, and a shear ratio of 17.9. Details of the polymerization test are shown in Table VI as Example 38.

EXAMPLE 39

8.49 grams of Ketjen Grade B alumina which had been calcined at 600°C in air for three hours was charged to a dry activator tube and heated under nitrogen to 300°C. 2.8 mls of thionyl chloride was then injected into the nitrogen upstream from the alumina. As it evaporated it was carried up through the alumina bed, reacting and chloriding the surface. When tested for polymerization activity this material provided 764 g/g/h of polymer having a melt index of 0.13, a high load melt index of 2.48, and a shear ratio of 18.6. Details of the polymerization test are shown in Table VI as Example 39.

EXAMPLE 40

7.63 grams of Ketjen Grade B alumina which had been calcined at 400°C in air for three hours was charged to a dry activator tube and heated under dry air to 300°C. 2.55 mls of sulfuryl chloride was then injected into the air upstream from the alumina. As it evaporated over a period of about 45 minutes at room temperature it was carried up through the alumina bed, reacting and chloriding the surface. When tested for polymerization activity this material provided 459 g/g/h of polymer having a melt index of 0.11, a high load melt index of 2.83, and a shear ratio of 25.6. Details of the polymerization test are shown in Table VI as Example 40.

COMPARATIVE EXAMPLES 41-43 AND EXAMPLES 44-45

2.6955 grams of solid aluminum trichloride was added to the reactor along with 2.0 mls of 15% triethyl aluminum and 2.0 mls of the metallocene solution used in previous experiments. Isobutane and ethylene were added as in previous

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runs. However, no activity was observed. This run is summarized in Table 6 as Example 41. The experiment was then repeated but with less aluminum trichloride in the reactor, but again no activity was observed. This was Example 42. Thus  $AlCl_3$  itself does not function as an activator for metallocenes. There is a distinct difference  
5 between aluminum trichloride and chlorided alumina.

In the following example aluminum trichloride was deposited onto the surface of dehydrated alumina in order to give it a higher surface area. 1.4 grams of anhydrous aluminum trichloride was dissolved in 100 mls of dichloromethane. This solution was then added to 6 grams of Ketjen Grade B alumina which had been  
10 calcined at 600°C in air for three hours. The dichloromethane was evaporated under nitrogen at 60°C. A sample of this material was then tested for polymerization activity (Example 43) but it had little. The material was then heated under nitrogen to 250°C for one hour and retested for polymerization activity (Example 44). This time some activity was detected. Next the material was again heated under nitrogen  
15 to 400°C for one hour and retested for polymerization activity (Example 45) and activity was observed.

#### COMPARATIVE EXAMPLES 46 AND 48 AND EXAMPLE 47

In another experiment 3.5 grams of Ketjen Grade B alumina calcined at 600°C was treated with 10 mls of 25% ethyl aluminum dichloride (EADC) at 60°C  
20 for 10 minutes, then rinsed twice to remove any unreacted EADC. When tested for polymerization activity (first without, then with cocatalyst), none was observed (Example 46). The material was then heated under nitrogen for 1 hour at 200°C and retested (Example 47). Some activity was observed.

In a similar experiment 4.31 grams of Ketjen Grade B alumina  
25 calcined at 400°C was treated with 30 mls of 25 wt% diethyl aluminum chloride (DEAC) at 90°C for 30 minutes. The excess DEAC was decanted and the solid washed three times in dry heptane. It was then dried at 100°C under nitrogen and tested for polymerization activity (Example 48). It exhibited 29.g/g/h activity.

#### COMPARATIVE EXAMPLE 49

30 A 2.26 gram sample of Davison 952 silica which had previously been calcined in dry air for three hours at 600°C was impregnated to the point of incipient wetness with 3.4 mls of trifluoromethane sulfonic acid (95.7% pure). The procedure

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was done under nitrogen in a flask. This material was then mixed with 8.96 grams of Ketjen Grade B alumina which had previously been calcined in dry air for three hours at 600°C. The resulting solid material was 79.9% by weight alumina, 29.1% by weight silica. This procedure was done in a dry activator tube on a fluidized bed  
5 in nitrogen. The mixture was heated to 193°C -230°C for three hours in nitrogen to allow the trifluoro-methane sulfonic acid to evaporate and react with the alumina, which would give a trifluoromethane sulfonic acid loading of 1 millimole per gram of the alumina. It was then tested for polymerization activity as described above except that the ethylene pressure was set at 450 psig instead of 550 psig and 25 mls of 1-  
10 hexene was added to the reactor. Results are shown in Table VII.

#### EXAMPLE 50

The solid oxide from Example 49 was then heated under nitrogen to 400°C for an additional three hours to further encourage distribution and reaction of the triflic acid. It was then tested for polymerization activity as described above  
15 except that the ethylene pressure was set at 450 psig instead of 550 psig and 25 mls of 1-hexene was added to the reactor. Results are shown in Table VII.

#### EXAMPLE 51

The solid oxide from Example 50 was again heated under nitrogen to 600°C for an additional three hours to further encourage distribution of the triflic  
20 acid. It was then tested for polymerization activity as described above except that the ethylene pressure was set at 450 psig instead of 550 psig and 25 mls of 1-hexene was added to the reactor. Results are shown in Table VII.

#### EXAMPLE 52

A solution of 0.5 grams of ammonium bifluoride was dissolved in 30  
25 mls of methanol and deposited onto a 4.5 gram sample of Ketjen Grade B alumina which had been calcined at 600°C for three hours in air. This brought the solid just beyond the point of incipient wetness. The methanol was then evaporated off under a nitrogen purge on a hot plate and then transferred to an activator tube, where it was heated under nitrogen to 500°C and held 2 hours. 1.89 grams of this material was  
30 then treated at 500C under nitrogen with 0.5 mls of carbon tetrachloride injected into the gas stream. A sample was then tested for polymerization activity with metallocene and 2.0 mls of triethyl aluminum cocatalyst. It generated 3132 g/g/h of



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polymer. Details are listed in Table VIII.

#### EXAMPLE 53-54

6.18 grams of W.R.Grace Grade HPV alumina which had been calcined at 600°C for three hours in air yielding a surface area of approximately 500 square meters per gram and a pore volume of about 2.8 cc/g, was transferred to a dry activator tube and heated under nitrogen to 600°C. 0.24 mls of perfluorohexane was then injected into the nitrogen stream ahead of the furnace. The liquid evaporated and was carried up through the alumina bed, fluoriding its surface. Then 1.55 mls of carbon tetrachloride was injected into the nitrogen stream and carried into the alumina bed at 600°C. The temperature was cooled to 25°C and the resultant fluorided-chlorided alumina was stored under nitrogen. A small sample of this material was then tested for polymerization activity with metallocene and triethyl aluminum. The activity, shown in Example 53, was quite high, at 4390 g/g/h.

This material was then run again except that it was allowed to stir in isobutane with the metallocene at 90°C for 30 minutes before the other ingredients were added. This procedure yielded 6298 g/g/h activity (Example 54).

#### EXAMPLE 55

Degussa Aluminoxid C, obtained by flame hydrolysis, was calcined at 600°C in air for three hours. Then 2.74 grams of this calcined alumina was heated to 600°C in air, into which 4.1 mls of perfluorohexane was injected. As the liquid evaporated, it was carried up by the air through the alumina bed. Afterwards the gas stream was switched from air to nitrogen and 1.0 ml of carbon tetrachloride was injected. After all had evaporated, the solid was cooled to room temperature and stored under dry nitrogen. A small sample was tested for polymerization activity with metallocene and cocatalyst as previously described. This material was found to yield 1383 g/g/h. Details are recorded in Table VIII.

#### EXAMPLES 56, 60-61, 63-64 AND COMPARATIVE

#### EXAMPLES 57-59, 62, 65-66.

A chlorided alumina was prepared identically to that in Example 33. In each experiment a sample of the oxide was added to the reactor under nitrogen, then 2 mls of a solution of 0.5 grams of bis(n-butyl cyclopentadienyl) zirconium dichloride in 100 mls of toluene was added, then 0.6 liter of isobutane liquid, then 1

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mmol of the cocatalyst (usually from a hexane solution) followed by another 0.6 liter of isobutane, and finally the ethylene was added after the reactor reached 90°C.

Table IX shows the results of these experiments as Examples 56 through 62.

5 A similar comparison of cocatalysts was made using an alumina which had been fluorided rather than chlorided according to the preparation used in Example 21. These runs are shown in Table IX in Examples 63 through 66.

#### EXAMPLES 67-71

10 In each run below the fluorided chlorided alumina used in Example 50 was charged to the reactor, followed by 2 mls of a solution of 0.5 grams of the selected metallocene in 100 mls of toluene, followed by 0.6 liter of isobutane liquid, then 2.0 mls of 1M triethyl aluminum as cocatalyst, followed by another 0.6 liters of isobutane and finally the ethylene. These runs were made at 90°C, like all previous runs. Details are shown in Table X.

TABLE I

Ex. #	A <sup>1</sup>	°C <sup>2</sup>	S <sup>3</sup>	OAC <sup>4</sup>	P <sup>5</sup>	T <sup>6</sup>	A <sup>7</sup>
1 <sup>8</sup>	None	NA	0.0000	2 TEA	0	61.1	0
2	None	NA	0.0000	2 EADC	0	28.0	0
3	Silica	600	0.5686	2 TEA	0.65	63.0	1
4	Alumina	800	0.6948	1 TEA	2.7	30.7	8
5	Alumina	600	0.2361	2 TEA	6.9	60.9	29
6	Alumina	400	0.8475	1 TEA	trace	57.2	0
7	Alumino-Phosphate (0.8)	600	0.8242	1 TEA	45	66.0	50
8	Silica-Alumina	600	0.3912	1 TEA	8.3	40.0	32
9	Silica-Titania	600	0.1392	2 TEA	0	60.0	0

Table - I Notes

1. This is the untreated solid oxide compound used.
2. This is the calcining temperature.
3. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
4. This is the amount, in milliliters of organoaluminum compound used and the type of organoaluminum used. The TEA was a 15 weight percent solution of triethylaluminum in heptane.
5. This is the amount of polymer produced in grams.
6. This is the amount of time used in minutes.
7. This is the activity in gP/(gS•hr).
8. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane.

TABLE II

Ex.#	A <sup>1</sup>	S <sup>2</sup>	°C <sup>3</sup>	S <sup>4</sup>	OAC <sup>5</sup>	P <sup>6</sup>	T <sup>7</sup>	A <sup>7</sup>
10 <sup>9</sup>	Silica	12.7	400	1.3360	2	0	30.0	0
11	Alumina	12.7	400	1.5251	2	38.0	45.0	33
12	Alumina	12.7	750	0.2994	2	174.5	60.0	583
13A	Alumina	1.6	550	0.3474	1	385.5	48.0	1387
13B	Alumina	0.8	550	0.7468	2	242.0	60.0	324
13C	Alumina	0.8	800	0.8004	2	34.8	45.0	58
14A	Alumina	2.7	550	0.0842	2	241	60	2862
14B	Alumina	2.7	650	0.0801	2	203	60	2534
15	Alumina	1.5	550	0.0279	2	90	60	3226
16	Alumina	0.26	500	0.7749	2	2.3	30.0	6
17	Silica-Alumina	1.6	600	0.3318	1	19.0	42.0	82

Table - II Notes

1. This is the solid oxide compound used.
2. This is the amount of sulfate used in mmols sulfate per gram of solid oxide.
3. This is the calcining temperature.
4. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
5. This is the amount, in milliliters, of TEA used. It was a 15 weight percent solution of triethylaluminum in heptane.
6. This is the amount of polymer produced in grams.
7. This is the amount of time used in minutes.
8. This is the activity in gP/(gS•hr).
9. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n- butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane.

TABLE III

Ex.#	A <sup>1</sup>	S <sup>2</sup>	°C <sup>3</sup>	S <sup>4</sup>	OAC <sup>5</sup>	P <sup>6</sup>	T <sup>7</sup>	A <sup>8</sup>
18 <sup>9</sup>	Alumina	3.90	500	0.8284	2	296.8	23.2	927
19	Alumina	3.90	250	0.2542	2	7.6	40.0	45
20	Alumina	3.90	400	0.2358	2	88.1	60.0	374
21	Alumina	3.90	600	0.2253	2	281.6	60.0	1250
22	Alumina	5.80	500	0.2563	1	243.9	60.0	952
23	Alumina	55	500	0.2212	1	280.0	60.0	1266
24	Alumina	55	600	0.0855	1	187.5	60.5	2179

Table - III Notes

1. This is the solid oxide compound used.
2. This is the amount of fluoride used in mmols fluoride per gram of solid oxide.
3. This is the calcining temperature.
4. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
5. This is the amount, in milliliters, of TEA used. It was a 15 weight percent solution of triethylaluminum in heptane.
6. This is the amount of polymer produced in grams.
7. This is the amount of time used in minutes.
8. This is the activity in gP/(gS•hr).
9. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane.

TABLE IV

Ex.#	A <sup>1</sup>	°C <sup>2</sup>	S <sup>3</sup>	OAC <sup>4</sup>	P <sup>5</sup>	T <sup>6</sup>	A <sup>7</sup>
25 <sup>8</sup>	Alumina	600	0.2612	1	62.0	64.0	223
26	Alumina	600	0.1688	1	38.0	74.6	181
27	Alumina	600	0.2046	1	11.9	33.0	106

## Table - IV Notes

1. This is the solid oxide compound used.
2. This is the calcining temperature.
3. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
4. This is the amount, in milliliters, of TEA used. It was a 15 weight percent solution of triethylaluminum in heptane.
5. This is the amount of polymer produced in grams.
6. This is the amount of time used in minutes.
7. This is the activity in gP/(gS·hr).
8. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane.

TABLE V

Ex.#	A <sup>1</sup>	S <sup>2</sup>	°C <sup>3</sup>	S <sup>4</sup>	OAC <sup>5</sup>	P <sup>6</sup>	T <sup>7</sup>	A <sup>8</sup>
28 <sup>9</sup>	Alumina	15.5	400	0.1596	2	149.8	60.0	939
29	Alumina	15.5	400	0.1166	2	121.8	61.5	1019
30	Alumina	2.4	400	0.2157	2	28.8	55.0	146
31	Alumina	37.6	400	0.1021	2	123.9	62.0	1174
32	Alumina	11.7	250	0.4878	2	39.2	60.0	80
33	Alumina	11.7	600	0.2058	2	351.5	63.0	1627
34	Alumina	38.2	800	0.0488	1	30.6	46.5	809
35	Alumina	11.7	600	0.1505	1	400.0	62.0	2572
36	Alumina	39.3	600	0.0927	1	260.2	60.0	2807
37	Silica-Alumina	11.7	600	0.0667	1	147.8	60.5	2198

Table - V Notes

1. This is the solid oxide compound used.
2. This is the amount of chloride used in mmols chloride per gram of solid oxide.
3. This is the calcining temperature.
4. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
5. This is the amount, in milliliters, of TEA used. It was a 15 weight percent solution of triethylaluminum in heptane.
6. This is the amount of polymer produced in grams.
7. This is the amount of time used in minutes.
8. This is the activity in gP/(gS•hr).
9. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these examples were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane.

TABLE VI

Ex.#	A <sup>1</sup>	Treatment	S <sup>2</sup>	OAC <sup>3</sup>	P <sup>4</sup>	T <sup>5</sup>	A <sup>6</sup>
38 <sup>7</sup>	Alumina	SiCl <sub>4</sub> - 400°C	0.2013	1	116.5	60.0	579
39	Alumina	SOCl <sub>2</sub> - 300°C	0.0793	1	62.0	61.4	764
40	Alumina	SO <sub>2</sub> Cl <sub>2</sub> - 300°C	0.3915	1	186.0	62.1	459
41	none	AlCl <sub>3</sub> solid	2.6955	2	0	30.0	0
42	none	AlCl <sub>3</sub> solid	0.0380	2	0	34.4	0
43	Alumina	AlCl <sub>3</sub> - 80°C	0.4264	2	4.3	28.0	22
44	Alumina	AlCl <sub>3</sub> - 250°C	0.3374	2	135.3	60.0	401
45	Alumina	AlCl <sub>3</sub> - 400°C	0.2335	1	74.9	60.0	322
46	Alumina	EtAlCl <sub>2</sub> - 60°C	0.8855	2	0	30.0	0
47	Alumina	EtAlCl <sub>2</sub> - 200°C	0.8943	2	122.9	49.0	168
48	Alumina	Et <sub>2</sub> AlCl - 90°C	0.4263	1	4.9	24.0	29

## Table - VI Notes

1. This is the solid oxide compound used.
2. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
3. This is the amount, in milliliters, of TEA used. It was a 15 weight percent solution of triethylaluminum in heptane.
4. This is the amount of polymer produced in grams.
5. This is the amount of time used in minutes.
6. This is the activity in gP/(gS•hr).
7. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane.



TABLE VII

Ex.#	A <sup>1</sup>	S <sup>2</sup>	°C <sup>3</sup>	S <sup>4</sup>	OAC <sup>5</sup>	P <sup>6</sup>	T <sup>7</sup>	A <sup>8</sup>
49	Alumina	1.0	200	.0868	1	1.5	80.5	13
50	Alumina	1.0	400	.1530	1	95.1	60.5	616
51	Alumina	1.0	600	.0467	1	51.1	60.2	1090

## Table - VII Notes

1. This is the solid oxide compound used.
2. This is the amount of triflate used in mmols triflate per gram of solid oxide.
3. This is the calcining temperature.
4. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
5. This is the amount, in milliliters, of TEA used. It was a 15 weight percent solution of triethylaluminum in heptane.
6. This is the amount of polymer produced in grams.
7. This is the amount of time used in minutes.
8. This is the activity in gP/(gS•hr).
9. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 450 psig ethylene, in 1.2 liters of isobutane, and in 25 mls of 1-hexene.

TABLE VIII

EX.#	A <sup>1</sup>	Treatment	S <sup>2</sup>	OAC <sup>3</sup>	P <sup>4</sup>	R <sup>5</sup>	A <sup>6</sup>
52 <sup>7</sup>	Alumina	F/500C & Cl/500C	0.2822	2	294.6	20.0	3132
53	Alumina	F/600C & Cl/600C	0.0767	2	338.4	60.3	4390
54	Alumina	F/600C & Cl/600C	0.0967	2	304.5	30.0	6298
55	Alumina	F/600C & Cl/600C	0.1196	1	174.2	63.2	1383

## Table - VIII Notes

1. This is the solid oxide compound used.
2. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
3. This is the amount, in milliliters, of TEA used. It was a 15 weight percent solution of triethylaluminum in heptane.
4. This is the amount of polymer produced in grams.
5. This is the amount of time used in minutes.
6. This is the activity in gP/(gS•hr).
7. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane.

TABLE IX

Ex.#	A <sup>1</sup>	Treatment	S <sup>2</sup>	CC <sup>3</sup>	P <sup>4</sup>	T <sup>5</sup>	A <sup>6</sup>
56 <sup>7</sup>	Alumina	Chlorided	0.1866	AlEt3	336.0	60.0	1800
57	Alumina	Chlorided	0.1958	GaMe3	0	60.0	0
58	Alumina	Chlorided	0.1878	ZnEt2	0	60.0	0
59	Alumina	Chlorided	0.1756	MgBu2	2.5	60.0	14
60	Alumina	Chlorided	0.1966	AlEt2H	52.6	60.0	268
61	Alumina	Chlorided	0.1777	Al(1-Bu)3	293	60.0	1649
62	Alumina	Chlorided	0.1840	LiHex	0	60.0	0
63	Alumina	Fluorided	0.2253	AlEt3	281.6	60.0	1250
64	Alumina	Fluorided	0.2181	AlMe3	154.2	60.0	707
65	Alumina	Fluorided	0.2307	AlEt2Cl	0	40.0	0
66	Alumina	Fluorided	0.2465	BEt3	0	30.0	0

Table - IX Notes

1. This is the solid oxide compound used.
2. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
3. This is the amount, in milliliters, of cocatalyst used.
4. This is the amount of polymer produced in grams.
5. This is the amount of time used in minutes.
6. This is the activity in gP/(gS•hr).
7. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane.

TABLE X

Ex.#	A <sup>1</sup>	Treatment	S <sup>2</sup>	Metallocene <sup>6</sup>	P <sup>3</sup>	T <sup>4</sup>	A <sup>5</sup>
67	Alumina	F/Cl 600C	0.0212	A	141.3	63.3	6318
68	Alumina	F/Cl 600C	0.0170	B	31.1	66.3	1656
69	Alumina	F/Cl 600C	0.0213	C	15.8	64.2	693
70	Alumina	F/Cl 600C	0.1000	D	83.9	61.5	819

## Table - X Notes

1. This is the solid oxide compound used.
2. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
3. This is the amount of polymer produced in grams.
4. This is the amount of time used in minutes.
5. This is the activity in gP/(gS•hr).
6. A = bis(n-butylcyclopentadienyl) zirconium dichloride  
 B = bis(cyclopentadienyl) zirconium dichloride  
 C = bis(cyclopentadienyl) hafnium dichloride  
 D = bis(n-butylcyclopentadienyl) zirconium chloride trimethylsilylmethyl

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COMPARATIVE EXAMPLE 72

Ketjen Grade B alumina was calcined in fluidizing dry air as described in previous examples at 600°C for three hours, and stored under dry nitrogen. Then 9.3 grams of this material was again heated under fluidizing nitrogen to 600°C. At this temperature 2.3 mls of carbon tetrachloride was injected into the nitrogen stream ahead of the alumina. It evaporated over a period of several minutes and was carried up through the alumina bed, where it reacted to chloride treat the surface. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XI.

10 COMPARATIVE EXAMPLE 73

Ketjen Grade B alumina was slurried in isopropanol alcohol, to which sulfuric acid was added in an amount equivalent to 2.5% of the alumina weight. The alcohol was then evaporated off at about 100°C under vacuum overnight. A sample was then calcined in dry air as described above at 600°C for three hours. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XI.

EXAMPLE 74

A 24.68 gram sample of virgin Ketjen Grade B alumina was impregnated with a solution of 4.2 grams of cupric chloride dihydrate in 55 mls of deionized water. It was then dried overnight at 100°C under vacuum, pushed through a 35 mesh screen, and calcined in dry fluidizing air at 600°C for three hours in order to convert much of the chloride to a mixed oxide. 16.53 grams of this material was then calcined under fluidizing nitrogen at 600°C into which 4.3 mls of carbon tetrachloride was injected, as described above, in order to re-chlorinate the surface. This material was then stored under dry nitrogen and later tested for polymerization activity. It yielded 164 grams of polyethylene having a melt index of 0.17, a high load melt index of 4.02 and a HLMI/MI ratio of 23.6. Results are shown in Table XI.

EXAMPLE 75

30 A solution of 5.0 grams of cupric sulfate pentahydrate in 50 mls of deionized water was impregnated onto 20.0 grams of virgin Ketjen Grade B alumina. It was dried overnight under vacuum at 100°C, pushed through a 100 mesh screen,

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and calcined in fluidizing dry air at 600°C for three hours. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XI.

#### EXAMPLE 76

5           A 13.35 gram sample of the material described above in Example 13 was then calcined again under nitrogen at 600°C. Into the gas stream ahead of the sample was injected 3.4 mls of carbon tetrachloride which vaporized and was carried through the sample bed where it reacted. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XI.

#### 10           EXAMPLE 77

          A 9.0 gram sample of Ketjen Grade B alumina which had been previously calcined in air at 600°C for three hours was then impregnated with a solution 4.77 grams of anhydrous gallium trichloride dissolved in 24 mls of carbon tetrachloride. The solvent was evaporated on a hot plate under flowing nitrogen. A  
15   12.74 gram sample of this material was then calcined again under air at 600°C for three hours to convert much of the gallium chloride to a mixed oxide. The gas stream was then changed to nitrogen and ahead of the sample was injected 3.4 mls of carbon tetrachloride which vaporized and was carried through the sample bed where it reacted to re-chlorinate the surface. This material was then stored under dry  
20   nitrogen and later tested for polymerization activity. Results are shown in Table XII.

#### EXAMPLES 78 & 79

          A solution of 50 mls of heptane and 25 mls of tin tetrachloride liquid was impregnated onto a 50.0 gram sample of Ketjen Grade B alumina. The sample became warm and evolved HCl gas, indicating some reaction with moisture in the  
25   structure. It was then dried overnight under vacuum at 100°C and pushed through a 35 mesh screen. A portion of this material was then calcined in dry air at 600°C for three hours to convert some of the tin chloride species to a mixed oxide. Then 4.9 grams of this material was calcined at 600°C in dry nitrogen into which 1 ml of carbon tetrachloride was injected in order to re-chlorinate the surface. This material  
30   was then stored under dry nitrogen and later tested for polymerization activity. In one experiment it yielded 202 grams of polyethylene having a melt index of 0.16, a high load melt index of 3.27, a HLMI/MI ratio of 20.7, a weight average MW of

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174,000, a number average MW of 57,500, and Mw/Mn of 3.1. Results are shown in Table XII.

#### EXAMPLE 80

A solution of 60 mls of deionized water and 6.0 grams of silver nitrate  
5 was impregnated onto a 30.0 gram sample of Ketjen Grade B alumina. It was then  
dried overnight under vacuum at 100°C and pushed through a 35 mesh screen. A  
12.6 gram portion of this material was then calcined in dry air at 600°C for three  
hours to convert the silver species to a mixed oxide. Then the gas stream was  
changed to nitrogen while still at 600C and 1.9 mls of carbon tetrachloride was  
10 injected in order to chlorinate the surface. This material was then stored under dry  
nitrogen and later tested for polymerization activity. Results are shown in Table XII.

#### EXAMPLE 81

A solution of 9.0 grams of niobium pentaethoxide in 40 mls of  
isopropanol was impregnated onto a 20.0 gram sample of Ketjen Grade B alumina. It  
15 was then dried overnight under vacuum at 100°C and pushed through a 35 mesh  
screen. A 10.68 gram portion of this material was then calcined in dry air at 600°C  
for three hours to convert the niobium species to a mixed oxide. Then the gas stream  
was changed to nitrogen while still at 600°C and 1.6 mls of carbon tetrachloride was  
injected in order to chlorinate the surface. This material was then stored under dry  
20 nitrogen and later tested for polymerization activity. Results are shown in Table XII.

#### EXAMPLE 82

To 20 grams of a solution of 50% manganese dinitrate in water was  
added another 35 mls of deionized water. This solution was then impregnated onto a  
20.0 gram sample of Ketjen Grade B alumina. It was then dried overnight under  
25 vacuum at 100°C and pushed through a 35 mesh screen. A 9.61 gram portion of this  
material was then calcined in dry air at 600°C for four hours to convert the  
manganese species to a mixed oxide. Then the gas stream was changed to nitrogen  
while still at 600°C and 2.3 mls of carbon tetrachloride was injected in order to  
chlorinate the surface. This material was then stored under dry nitrogen and later  
30 tested for polymerization activity. Results are shown in Table XII.

#### EXAMPLE 83

A solution of 100 mls of deionized water and 20.0 grams of

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ammonium metatungstate was impregnated onto a 50.0 gram sample of Ketjen Grade B alumina. It was then dried overnight under vacuum at 100°C and pushed through a 35 mesh screen. A 15.43 gram portion of this material was then calcined in dry air at 600°C for three hours to convert the tungsten species to a mixed oxide. Then the gas stream was changed to nitrogen while still at 600°C and 2.35 mls of carbon tetrachloride was injected in order to chlorinate the surface. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XII.

#### EXAMPLE 84

A solution of 100 mls of deionized water and 25.0 grams of lanthanum trinitrate hexahydrate was impregnated onto a 50.0 gram sample of Ketjen Grade B alumina. It was then dried overnight under vacuum at 100°C and pushed through a 35 mesh screen. A 9.38 gram portion of this material was then calcined in dry air at 600°C for three hours to convert the lanthanum species to a mixed oxide. Then the gas stream was changed to nitrogen while still at 600°C and 2.4 mls of carbon tetrachloride was injected in order to chlorinate the surface. This material was then tested for polymerization activity where it produced 94.5 grams of polyethylene having a melt index of 0.14, a high load melt index of 2.43, and a HLMI/MI ratio of 17.6. Results are shown in Table XII.

#### EXAMPLE 85

A solution of 35 mls of deionized water and 7.29 grams of neodymium trichloride hexahydrate was impregnated onto a 23.53 gram sample of Ketjen Grade B alumina. It was then dried overnight under vacuum at 100°C and pushed through a 100 mesh screen. A portion of this material was then calcined in dry air at 600°C for three hours to convert the neodymium species to a mixed oxide. Then 10.2 grams of this material was heated under nitrogen to 600°C again and while still at 600°C 2.5 mls of carbon tetrachloride was injected in order to re-chlorinate the surface. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XII.

#### COMPARATIVE EXAMPLE 86

A 2.9 gram sample of Ketjen Grade B alumina which had previously been calcined in dry air for three hours at 600°C, was moistened with 7.5 mls of



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dichloromethane. Then 2.9 mls of a 1 molar solution of antimony pentachloride in dichloromethane was added to form a slurry. The solvent was then evaporated off under flowing nitrogen on a hot plate. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XII.

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EXAMPLE 87

A 1.55 gram sample of the material from Example 23 was calcined at 600°C in air for one hour to convert some of the antimony species to a mixed oxide. Then the gas stream was changed to nitrogen while still at 600°C and 0.4 mls of carbon tetrachloride was injected in order to re-chlorinate the surface. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XII.

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COMPARATIVE EXAMPLE 88

Ketjen Grade B alumina was calcined at 600°C in air for three hours. Then 10.42 grams of this material was again calcined under 600°C nitrogen. 2.6 mls of carbon tetrachloride was injected in order to chlorinate the surface. This material was then stored under dry nitrogen and later tested for polymerization activity. It yielded 280 grams of polyethylene having a density of 0.9410, a melt index of 0.61, a high load melt index of 9.87, and a HLMI/MI ratio of 16.2. Results are shown in Table XIII.

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COMPARATIVE EXAMPLE 89

A 4.5 gram sample of Ketjen Grade B alumina which had previously been calcined in dry air for three hours at 600°C, was slurried in a solution of 0.5 grams ammonium bifluoride in 30 mls of methanol. The solvent was then evaporated off under flowing nitrogen on a hot plate. The resultant solid was then calcined in nitrogen at 500°C for two hours. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XIII.

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EXAMPLE 90

A solution of 40 mls of deionized water and 2.0 grams of zinc dichloride was made. A few drops of nitric acid had to be added to dissolve all the zinc. This solution was then impregnated onto a 10 gram sample of Ketjen Grade B alumina. Thus the zinc chloride loading was 20% of the alumina. It was then dried overnight under vacuum at 100°C and pushed through a 100 mesh screen. A portion

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of this material was then calcined in dry air at 600°C for three hours to convert the zinc species to a mixed oxide. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XIII.

#### EXAMPLE 91

5           A solution of 35 mls of deionized water and 1.9 grams of zinc chloride was made. A few drops of nitric acid had to be added to dissolve all of the zinc. This solution was then impregnated onto a 18.35 gram sample of Ketjen Grade B alumina. Thus the zinc chloride loading was 10% of the alumina. It was then dried overnight under vacuum at 100°C and pushed through a 100 mesh screen. A portion  
10 of this material was then calcined in dry air at 600°C for three hours to convert the zinc species to a mixed oxide. Then 11.37 grams of this material was heated under nitrogen to 600°C again and while still at 600°C 2.85 mls of carbon tetrachloride was injected in order to chlorinate the surface. This material was found to have a pore volume of 0.90 cc/g and a surface area of 248 square meters per gram. It was then  
15 stored under dry nitrogen and later tested for polymerization activity. It yielded 158 grams of polyethylene having a density of 0.9406. Results are shown in Table XIII.

#### EXAMPLE 92

          A solution of 435 mls of deionized water, 34.65 grams of zinc chloride, and 2.5 mls of nitric acid was made and impregnated onto a 170.35 gram  
20 sample of Ketjen Grade B alumina. Thus the zinc chloride loading was 20% of the alumina. It was then dried overnight under vacuum at 100°C and pushed through an 80 mesh screen. A portion of this material was then calcined in dry air at 600°C for three hours to convert the zinc species to a mixed oxide. Then 25.96 grams of this material was heated under nitrogen to 600°C again and while still at 600C 2.4 mls of  
25 carbon tetrachloride was injected in order to chlorinate the surface. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XIII.

#### EXAMPLE 93

          A solution of 100 mls of deionized water, 13.03 grams of zinc  
30 chloride, and a few drops of nitric acid was made and impregnated onto 64.84 grams of Ketjen Grade B alumina. Thus the zinc chloride loading was 20% of the alumina. It was then dried overnight under vacuum at 100°C and pushed through a 100 mesh

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screen. A portion of this material was then calcined in dry air at 600°C for three hours to convert the zinc species to a mixed oxide. Then 35.94 grams of this material was heated under nitrogen to 600°C again and while still at 600°C, 5.5 mls of carbon tetrachloride was injected in order to chlorinate the surface. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XIII.

#### EXAMPLE 94

A solution of 43 mls of deionized water, 7.3 grams of zinc chloride, and a few drops of nitric acid was made and impregnated onto a 17.24 gram sample of Ketjen Grade B alumina. Thus the zinc chloride loading was 40% of the alumina. It was then dried overnight under vacuum at 80°C and pushed through an 100 mesh screen. A portion of this material was then calcined in dry air at 600°C for three hours to convert the zinc species to a mixed oxide. Then 12.47 grams of this material was heated under nitrogen to 600°C again and while still at 600°C 3.1 mls of carbon tetrachloride was injected in order to chlorinate the surface. It was found to have a pore volume of 0.89 cc/g and a surface area of 217 square meters per gram. This material was then stored under dry nitrogen and later tested for polymerization activity. It yielded 157.8 grams of polyethylene having a melt index of 0.69, a high load melt index of 11.4, and a HLMI/MI ratio of 16.5. Results are shown in Table XIII.

#### COMPARATIVE EXAMPLE 95

A solution of 50 mls of deionized water, 4.0 grams of zinc chloride, and a few drops of nitric acid was made and impregnated onto a 20.0 gram sample of W.R.Grace Grade 952 silica. Thus the zinc chloride loading was 20% of the alumina. It was then dried overnight under vacuum at 80°C and pushed through an 100 mesh screen. A portion of this material was then calcined in dry air at 600°C for three hours to convert the zinc species to a mixed oxide. Then 19.08 grams of this material was heated under nitrogen to 600°C again and while still at 600°C 4.8 mls of carbon tetrachloride was injected in order to chlorinate the surface. This material was then stored under dry nitrogen and later tested for polymerization activity. Results are shown in Table XIII.

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EXAMPLE 96

A portion of the material created in Example 28 was calcined in dry air at 600°C for three hours to convert the zinc species to a mixed oxide. Then 4.4 grams of this material was heated under air to 600°C again and while still at 600°C  
5 2.9 mls of perfluorohexane was injected in order to fluoridate the surface. This material was then stored under dry nitrogen and later tested for polymerization activity. It yielded 124.5 grams of polyethylene having a melt index of 0.99, a high load melt index of 16.5, a HLMI/MI ratio of 16.5, and a density of 0.9408. Results are shown in Table XIII.

10

EXAMPLE 97

A 3.0 gram portion of the material created in Example 34 was calcined in dry nitrogen at 600°C and while still at 600°C 0.75 ml of carbon tetrachloride was injected in order to chlorinate the surface. This material was then stored under dry  
15 polyethylene having a melt index of 0.54, a high load melt index of 9.2, a HLMI/MI ratio of 17.0, and a density of 0.9401. Results are shown in Table XIII.

TABLE XI

Ex.#	Metal	Anion	°C <sup>1</sup>	S <sup>2</sup>	OAC <sup>3</sup>	P <sup>4</sup>	T <sup>5</sup>	A <sup>6</sup>
72	none	Cl	600	0.2058	2	351.5	63.0	1627
73	none	SO <sub>4</sub>	600	0.7749	2	2.3	30.0	3
74	Cu	Cl	600	0.0653	1	164.0	60.0	2966
75	Cu	SO <sub>4</sub>	600	0.2045	1	89.1	71.6	365
76	Cu	Cl & SO <sub>4</sub>	600	0.0523	1	283.4	60.3	4526

Table - XI Notes

1. This is the calcining temperature.
2. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
3. This is the amount, in milliliters of organoaluminum compound used and the type of organoaluminum used. The TEA was a 15 weight percent solution of triethylaluminum in heptane.
4. This is the amount of polymer produced in grams.
5. This is the amount of time used in minutes.
6. This is the activity in gP/(gS•hr).
7. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane.

TABLE XII

Ex.#	Metal	°C	S <sup>2</sup>	PC <sup>7</sup>	OAC <sup>3</sup>	P <sup>4</sup>	T <sup>5</sup>	A <sup>6</sup>
77	Ga	600	0.0543	1	1	200.3	60.0	3115
78	Sn	600	0.0360	1	1	202.0	71.1	4735
79	Sn	600	0.1349	1	1	157.3	10.2	6859
80	Ag	600	0.0659	1	1	340.0	60.0	5159
81	Nb	600	0.0657	1	1	139.1	62.4	2036
82	Mn	600	0.0472	1	1	72.8	61.4	1507
83	W	600	0.0320	1	1	106.9	61.0	3286
84	La	600	0.868	1	1	94.5	61.7	1059
85	Nd	600	0.0473	2	1	55.8	61.1	1158
86	Sb	none	0.3319	1	1	0	60.0	0
87	Sb	600	0.0716	1	1	166.4	61.2	2272

Table - XII Notes

1. This is the calcining temperature.
2. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
3. This is the amount, in milliliters of organoaluminum compound used and the type of organoaluminum used. The TEA was a 15 weight percent solution of triethylaluminum in heptane.
4. This is the amount of polymer produced in grams.
5. This is the amount of time used in minutes.
6. This is the activity in gP/(gS•hr).
7. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane (condition 1) or 450 psig and 25 mild 1-hexene (condition 2).

TABLE- XIII

Ex.#	Metal	Anion	°C <sup>1</sup>	S <sup>2</sup>	PC <sup>7</sup>	OAC <sup>3</sup>	P <sup>4</sup>	T <sup>5</sup>	A <sup>7</sup>
88	none	Cl	600	0.2005	2	1	280.0	61.5	1362
89	none	F	500	0.8284	1	2	296.8	23.2	927
90	Zn 20%	none	600	0.2475	1	1	17.4	35.4	119
91	Zn 10%	Cl	600	0.0567	2	1	158.0	60.0	2787
92	Zn 20%	Cl	600	0.0376	2	1	209.6	64.6	5178
93	Zn 20%	Cl	600	0.0120	1	1	141.6	60.0	11800
94	Zn 40%	Cl	600	0.0313	2	1	157.8	62.8	4817
95	Zn 20%	Cl	600	0.2860	2	1	0.3	76.9	1
96	Zn 20%	F	600	0.0677	2	1	124.5	60.0	1839
97	Zn 20%	F & Cl	600	0.0240	2	1	68.5	63.0	2718

Table - XIII Notes

1. This is the calcining temperature.
2. This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
3. This is the amount, in milliliters of organoaluminum compound used and the type of organoaluminum used. The TEA was a 15 weight percent solution of triethylaluminum in heptane.
4. This is the amount of polymer produced in grams.
5. This is the amount of time used in minutes.
6. This is the activity in gP/(gS•hr).
7. The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90°C, under 550 psig ethylene, in 1.2 liters of isobutane (condition 1) or 450 psig and 25 mild 1-hexene (condition 2).

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C L A I M S

1. A process for producing a catalyst composition for polymerizing monomers, said process comprising contacting an organometal compound, a treated solid oxide compound, and an organoaluminum compound to produce said  
5 composition,

wherein said composition comprises a post-contacted organometal compound and a post-contacted treated solid oxide compound;

wherein said composition can polymerize ethylene into a polymer with an activity greater than a composition that uses the same organometal compound, and  
10 the same organoaluminum compound, but uses untreated Ketjen grade B alumina instead of said treated solid oxide compound;

wherein said organometal compound has the following general formula:



15 wherein  $M^1$  is titanium, zirconium, or hafnium, and wherein  $(X^1)$  is independently a Group OMC-I radical which is a cyclopentadienyl, an indenyl, a fluorenyl, a substituted cyclopentadienyl, a substituted indenyl, or a substituted fluorenyl, and wherein each said substituent on said substituted cyclopentadienyl, said substituted indenyl, or said substituted fluorenyl, is an aliphatic group, a cyclic group,  
20 a combination of said aliphatic and cyclic groups, an organometallic group, or hydrogen;

wherein  $(X^3)$  and  $(X^4)$  are independently a Group OMC-II radical which is a halide, an aliphatic group, a cyclic group, a combination of aliphatic and cyclic groups, or an organometallic group;

25 wherein  $(X^2)$  is a Group OMC-I or a Group OMC-II radical;  
wherein said organoaluminum compound has the following general formula:



30 wherein  $(X^5)$  is a hydrocarbyl having from 1-20 carbon atoms,  
wherein  $(X^6)$  is a halide, a hydride, or an alkoxide,  
wherein "n" is a number from 1 to 3 inclusive; and  
wherein the treated solid oxide compound is produced by contacting at



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least one solid oxide compound with at least one electron-withdrawing anion source compound to form a mixture.

2. A process according to claim 1, wherein the composition thus-produced consists essentially of the post-contacted compounds.

5 3. A process according to claim 1, wherein the composition thus-produced further comprises a post-contacted organoaluminum compound.

4. A process according to claim 3, wherein the composition thus-produced consists essentially of the post-contacted compounds.

5. A process according to claim 1, wherein said contacting of said at least  
10 one solid oxide compound with said at least one electron-withdrawing anion source compound further includes the presence of at least one metal salt compound.

6. A process according to claim 1, wherein producing the treated solid oxide compound includes calcining said mixture of said at least one solid oxide compound and said at least one electron-withdrawing anion source compound.

15 7. A process according to claim 1, wherein the treated solid oxide compound is produced by contacting and calcining simultaneously said at least one solid oxide compound with said at least one electron-withdrawing anion source compound.

8. A process according to claim 1, wherein said solid oxide compound is  
20 contacted with two or more electron-withdrawing anion source compounds in two or more separate contacting steps.

9. A process according to claim 1, wherein said composition can  
polymerize ethylene into a polymer with an activity greater than 100 (gP/(gS•hr));  
and wherein said treated solid oxide compounds comprise oxygen and at least one  
25 element of group 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 of the periodic table,  
including lanthanides and actinides.

10. A process according to 9, wherein said activity is greater than 250.

11. A process according to claim 10, wherein said activity is greater than  
500.

30 12. A process according to claim 11, wherein said activity is greater than  
1000.

13. A process according to according to claim 12, wherein said activity is

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greater than 2000.

14. A process according to claim 1, wherein said organometal compound is bis(cyclopentadienyl) hafnium dichloride, bis(cyclopentadienyl) zirconium dichloride, [ethyl(indenyl)<sub>2</sub>] hafnium dichloride, [ethyl(indenyl)<sub>2</sub>] zirconium dichloride, [ethyl (tetrahydroindenyl)<sub>2</sub>] hafnium dichloride, [ethyl(tetrahydroindenyl)<sub>2</sub>] zirconium dichloride, bis(n-butylcyclopentadienyl) hafnium dichloride, bis(n-butylcyclopentadienyl) zirconium dichloride, ((dimethyl)(diindenyl) silane) zirconium dichloride, ((dimethyl)(diindenyl) silane) hafnium dichloride, ((dimethyl) (ditetrahydro-indenyl) silane) zirconium dichloride, ((dimethyl)(di(2-methyl indenyl)) silane) zirconium dichloride, or bis(fluorenyl) zirconium dichloride;

wherein said organoaluminum compound is trimethylaluminum, triethylaluminum, tripropylaluminum, diethylaluminum ethoxide, tributylaluminum, triisobutylaluminum hydride, triisobutylaluminum or diethylaluminum chloride; and

- wherein said solid oxide compound is Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, BeO, Bi<sub>2</sub>O<sub>3</sub>, CdO, Co<sub>3</sub>O<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>, CuO, Fe<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, NiO, P<sub>2</sub>O<sub>5</sub>, Sb<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, SnO<sub>2</sub>, SrO, ThO<sub>2</sub>, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, ZnO, ZrO<sub>2</sub>, or a mixture of any two or more of said solid oxide compounds, wherein said treated solid oxide has been treated with fluoride or chloride or both.

15. A catalyst composition when produced by a process according to any one of the preceding claims:

16. A process for polymerizing a monomer which comprises contacting at least one monomer under polymerization conditions with a catalyst composition according to claim 15 to provide a polymer.

17. A process according to claim 16, which is conducted under slurry polymerization conditions.

18. A process according to claim 17, wherein said polymerization is conducted in a loop reactor.

19. A process according to claim 18, wherein said polymerization is conducted in the presence of a diluent that comprises, in major part, isobutane.

20. A process according to claim 16, wherein the polymer thus-produced is formed into a manufacture.

21. A process according to claim 20, wherein said manufacture is used to

form at least part of a machine.

22. A process for producing a catalyst composition substantially as herein described.
23. A process for producing a catalyst composition substantially as herein described with reference to any of the Examples.
24. A catalyst composition according to claim 15, substantially as herein described.
25. A catalyst composition according to claim 15, substantially as herein described with reference to any of the Examples.
- 10 26. A process for polymerizing a monomer according to claim 16, substantially as herein described.
27. A process for polymerizing a monomer according to claim 16, substantially as herein described with reference to any of the Examples.

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 99/06373

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08F4/642 C08F4/02 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 628 574 A (TOSOH CORP) 14 December 1994 (1994-12-14)</p> <p>example 1 column 7, line 6 - line 9 column 7, line 21 - line 35 example 2</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/--</p>	<p>1-6, 9-14, 22-27</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "S" document member of the same patent family

Date of the actual completion of the international search

14 July 1999

Date of mailing of the international search report

29. 07. 1999

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# INTERNATIONAL SEARCH REPORT

International Application No

PL US 99/06373

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>SOGA K ET AL: "ACTIVATION OF            SiO<sub>2</sub>-SUPPORTED ZIRCONOCENE CATALYSTS BY            COMMON TRIALKYLALUMINIUMS"            MAKROMOLEKULARE CHEMIE, MACROMOLECULAR            CHEMISTRY AND PHYSICS,            vol. 194, no. 12,            1 December 1993 (1993-12-01), pages            3499-3504, XP000411898            ISSN: 0025-116X            page 3500, paragraph 2            page 3503; example 21; table 5            table 6            page 3503, paragraph 4            -----</p>	<p>1-5,            15-17,            22-27</p>

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 99/06373

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 20, 21  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 99/06373

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 20,21

Claims 20 and 21 are depending on claim 1 and should therefore relate to a polymerisation process, which is not the case: claim 20 is a further manufacturing process claim and claim 21 is a use claim of the product obtained according to claim 20! These 2 claims are inconsistent and have not been searched.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/06373

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0628574 A	14-12-1994	JP 6345806 A	20-12-1994
		DE 69407094 D	15-01-1998
		DE 69407094 T	02-07-1998
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